[Contribution from the Department of Chemistry of the Pennsylvania State College]

ATTEMPTED REACTION OF 2-METHYL-1-VINYLCYCLOHEXENE WITH QUINONE[1]

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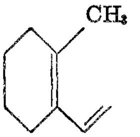
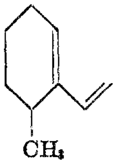
Received May 26, 1952

The Diels-Alder reaction between 2-methyl-1-vinylcyclohexene (I) and maleic anhydride has been investigated by three groups (1–3). Wang and Hu (3) recognized that the previous work had employed impure samples of diene and that the adducts which had been isolated actually resulted from the reaction of 6-methyl-1-vinylcyclohexene (II) with the maleic anhydride. Wang and Hu then claimed to have prepared the true adduct of I with maleic anhydride. In view of the unexpectedly high boiling point reported for I by these workers, doubt is cast on the structure of their adduct. We have been unable to isolate adducts from the reaction of diene I with either maleic anhydride or quinone, even when temperatures up to 180° were employed.[2, 3]

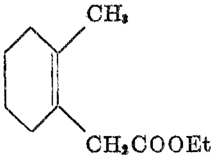
A mixture of 75% I and 25% II was prepared in five steps in 37% over-all yield from *o*-methylcyclohexanone. The ketone was condensed with ethyl bromoacetate in the presence of zinc, and the Reformatsky ester was dehydrated with thionyl chloride in pyridine. It seems most probable that the mixture of two compounds arose at this point and that the dehydrated product was 75% III and 25% IV. The two unsaturated esters were reduced with lithium aluminum hydride, converted to the acetate, and cracked at 600° to give the mixture of 75% I and 25% II.



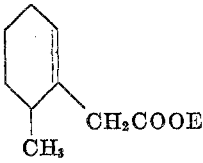
I



II



III



IV

The constitution of this mixture of dienes was inferred from the fact that under a variety of conditions the yield of adduct (V) with quinone was always 20–25%, and that the adduct was derived entirely from II. The reaction with maleic anhydride gave similar results. This ratio of dienes was supported by the ultraviolet absorption spectrum which showed peaks at 233 mμ and 229 mμ, thereby agreeing with those calculated (232 mμ and 227 mμ) for I and II by the use of Woodward's rules (4).

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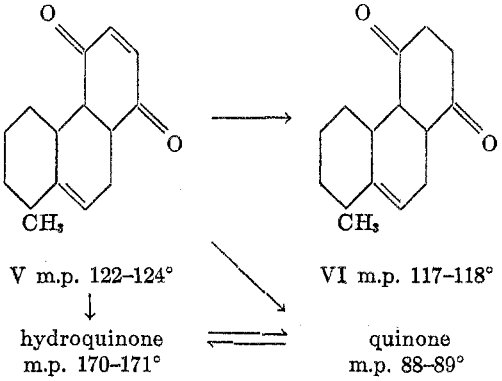
[1] This work was supported by a research grant from Bristol Laboratories, Inc.

[2] Dr. James Walker has informed us that he has also found that I fails to react with quinone.

[3] Added in Proof (Oct. 7, 1952): Since this article was submitted, Robins and Walker have reported the adduct of II with quinone [*J. Chem. Soc.*, 1610 (1952)]. We are happy to corroborate their result.

The adduct with quinone (V) was proven to be derived from II by degradation with zinc and then sulfur to 1-methylphenanthrene. The adduct was rearranged to the corresponding hydroquinone and oxidized to the corresponding quinone. These two compounds were interconverted. Reduction of the conjugated double bond in V was also successful in giving VI. The stereochemical configurations of these compounds can be tentatively assigned by the same arguments used for the adduct of quinone with 1-vinylcyclohexene (5).



V m.p. 122–124°

VI m.p. 117–118°

hydroquinone m.p. 170–171°

quinone m.p. 88–89°

EXPERIMENTAL

2-Methyl-1-vinylcyclohexene (I) *and 6-methyl-1-vinylcyclohexene* (II). *o*-Methylcyclohexanone was converted to the mixture of unsaturated esters (III and IV) by the method of Chuang, Tien, and Ma (6). The unsaturated esters were reduced to the unsaturated alcohols in 87% yield with lithium aluminum hydride in ether. The unsaturated alcohol mixture had the following properties: b.p. 100–104°/12 mm.; n_D^{15} 1.4927. The unsaturated alcohols were converted to the acetates (b.p. 106–107°/11 mm.; n_D^{20} 1.4685) in 86% yield. The acetates were cracked by distilling them through a glass tube heated to 600°. The yield of dienes (b.p. 76–77°/40 mm.; n_D^{20} 1.4938–1.4972) was 70–92% in conversions of 11–40%.

4a,4b,5,6,7,8,10,10a-Octahydro-8-methyl-1,4-phenanthrenequinone (V). The mixture of methylvinylcyclohexenes (I and II) (3 g., 0.0246 mole) was added to 3.0 g. (0.0278 mole) of quinone dissolved in 50 ml. of methanol. The solution was stirred briefly and allowed to stand 12 hours. Water was added to give 1.45 g. (25%) of large pale-yellow crystals of 4a,4b,5,6,7,8,10,10a-octahydro-8-methyl-1,4-phenanthrenequinone (V), m.p. 118–122°. Recrystallization from methanol gave colorless prisms, m.p. 122–124°.

Anal. Calc'd for $C_{15}H_{18}O_2$: C, 78.2; H, 7.88.

Found: C, 78.2; H, 8.09.

Similar yields were obtained when the reaction was conducted in refluxing benzene or in alcohol solutions. Treating the unreacted diene with quinone or maleic anhydride up to 180° failed to yield an isolatable adduct.

Conversion to 1-methylphenanthrene. The adduct (V) (500 mg.) was heated at 250–270° for two hours in a mixture of 0.5 g. of sodium chloride, 0.5 g. of zinc chloride, and 2.5 g. of zinc dust. The mixture was cooled and extracted with benzene and water. The benzene extract was evaporated to dryness and then heated at 200–220° for two hours with 1.5 g. of sulfur. The reaction mixture was distilled to give an orange gum, b.p. 120–130° at 0.1 mm. The gum was dissolved in benzene and passed through a short column of alumina to give 85 mg. (20%) of pale yellow needles of 1-methylphenanthrene, m.p. 107–110°. Recrystallization from methanol raised the m.p. to 116–119°, with no depression when mixed with an authentic sample.

4b,5,6,7,8,10-Hexahydro-8-methyl-1,4-dihydroxyphenanthrene. The initial adduct (V) (50 mg.) was dissolved in 5 ml. of ethanol and one drop of concentrated hydrochloric acid was added. The solution was warmed on the steam-bath for ten minutes and then water was added to give 40 mg. (80%) of colorless needles of 4b,5,6,7,8,10-hexahydro-8-methyl-1,4-dihydroxyphenanthrene, m.p. 166–169°. Sublimation at 90–100° and 0.1 mm. raised the m.p. to 170–171°.

Anal. Calc'd for $C_{15}H_{18}O_2$: C, 78.2; H, 7.88.

Found: C, 78.6; H, 8.26.

4b,5,6,7,8,10-Hexahydro-8-methyl-1,4-phenanthrenequinone. A solution of 1 g. of the original adduct (V) and 0.25 g. of selenium dioxide in 50 ml. of dioxane was refluxed for six hours. Then 50 ml. of water was added and the solution was evaporated to about 20 ml. A mixture of selenium and yellow needles separated. The precipitate was dissolved in ethanol and filtered to remove selenium. Addition of water gave 510 mg. of yellow needles, m.p. 68–74°. The product was contaminated with selenium, and after five recrystallizations from ethanol, traces of selenium still remained in the product. Distillation at 80–85° and 0.15 mm. and crystallization from methanol gave 432 mg. (44%) of yellow needles of 4b,5,6,7,8,-10-hexahydro-8-methyl-1,4-phenanthrenequinone, m.p. 88–89°.

Anal. Calc'd for $C_{15}H_{16}O_2$: C, 78.9; H, 7.06.

Found: C, 79.1; H, 6.46.

Oxidation of 4b,5,6,7,8,10-hexahydro-8-methyl-1,4-dihydroxyphenanthrene. The hydroquinone was oxidized to the quinone by the method employed by Fieser with other hydroquinones (7). Sodium nitrite was added to 435 mg. of the hydroquinone in 25 ml. of glacial acetic acid. The solution was warmed on the steam-bath during the addition. When the solution remained yellow after expulsion of oxides of nitrogen, the addition was stopped.

A solution of 150 mg. of sodium dichromate in 10 ml. of 5% sulfuric acid was then added to the reaction mixture. The solution was warmed on the steam-bath for 30 minutes and then cooled. Extraction with ether and evaporation of the ether gave an orange gum. Crystallization from methanol gave mixed gum and crystals. Sublimation at 80–100° and 0.2 mm. gave 76 mg. (17%) of yellow needles of the quinone, m.p. 88–89°.

Reduction of 4b,5,6,7,8,10-hexahydro-8-methyl-1,4-phenanthrenequinone. The quinone (50 mg.) was dissolved in 10 ml. of 50% acetic acid to give a yellow solution. Solid sodium hyposulfite was added with stirring until the solution was colorless. (A transient green color was observed, and if the solution was allowed to stand in the presence of air, it slowly changed back to green.) Evaporation of the reaction mixture under reduced pressure gave 26 mg. (52%) of colorless needles of the hydroquinone, m.p. 165–169°.

2,3,4a,4b,5,6,7,8,10,10a-Decahydro-8-methyl-1,4-phenanthrenequinone. The initial adduct (V) (300 mg.) was dissolved in 20 ml. of glacial acetic acid and 0.5 g. of zinc dust was added. The mixture was shaken vigorously for five minutes and then filtered. The filtrate was evaporated to dryness and the residue extracted with benzene. Evaporation of the benzene gave mixed crystals of needles and prisms. Recrystallization from methanol gave 108 mg. of long needles of the dione (VI), m.p. 116–118°. Recrystallization from methanol raised the melting point to 117–118°.

Anal. Calc'd for $C_{15}H_{20}O_2$: C, 77.5; H, 8.66.

Found: C, 77.1; H, 8.66.

SUMMARY

Several attempts to effect a Diels-Alder reaction between 2-methyl-1-vinylcyclohexene (I) and quinone failed. In the preparation of I, an isomeric diene 6-methyl-1-vinylcyclohexene (II) is also formed, which reacts readily with quinone. The structure of this adduct was proven and several of its reactions were investigated.

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(6) Chuang, Tien, and Ma, *Ber.*, **69**, 1494 (1936).
(7) Fieser, *J. Am. Chem. Soc.*, **70**, 3165 (1948).